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Syntheses of 2,9-Bis(halomethyl)-1,10-phenanthrolines: Potential Robust Ligands for Metal Oxidation Catalysts

Robert H. Beer, Jose Jimenez, and Russell S. Drago*

Department of Chemistry, University of Florida, Gainesville, Florida 32611

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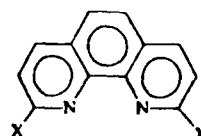
Free radical halogenation of 2,9-dimethyl-1,10-phenanthroline with *N*-bromosuccinimide and *N*-chlorosuccinimide form the known α -methyl derivatives 2,9-bis(trihalomethyl)-1,10-phenanthrolines. The compound 2,9-bis(trichloromethyl)-1,10-phenanthroline can be used for one-step syntheses of oxidatively resistant fluoro- and partially reduced chloromethyl derivatives capable of coordination to metal oxidation catalysts.

The functionalization of ligands with halogen substituents, particularly fluorine, enhance and prolong the activity of metal oxidation catalysts.¹ The *cis*-[Ru^{II}(CH₃CN)₂(1)₂]²⁺ complex, Chart I, where 1 is 2,9-dimethyl-1,10-phenanthroline, activates dioxygen and hydrogen peroxide for hydrocarbon oxygenation including methane.² Methods for functionalization of the methyl substituents of 1 with halogens have been developed to incorporate the phenanthroline subunit into polydentate and macrocyclic ligands.³ Our interest in the methyl substituents of 1, which are critical for the catalytic activity of *cis*-[Ru^{II}(CH₃CN)₂(1)₂]²⁺,^{2b} is the impact of halogenation on the activity and regioselectivity of the ruthenium and related catalysts. The syntheses of 2-5 from 1 have been accomplished previously by direct free radical halogenation or multistep syntheses.³ We report several modified routes to 2-5, and the first preparation of fluorinated derivative 6 (Chart I).

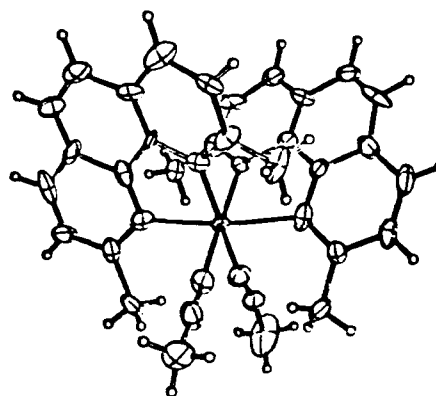
Results and Discussion

Treatment of commercially available 1 with excess *N*-bromosuccinimide (NBS) and *N*-chlorosuccinimide (NCS) afforded 2 and 3 by modification of the previous synthesis of 3.^{3b} Attempts to use stoichiometric amounts of NCS or Cl₂ produced primarily 3 or complex mixtures of products in accord with previous reports of free radical halogenation of 1.^{3a,b} Practically no reaction of [Zn(1)-Cl₂]⁴ with NCS occurred under the same conditions, yielding only minor amounts of mono- and disubstituted chlorinated products 4 and 5.^{3b,c} A correlation has been shown between chlorination and the electronic environment of the methyl substituent of heterocycles.⁵ Though steric effects may also play a role in the surprising lack of reactivity of coordinated 1, these results suggest that the

Chart I



X, X' = CH₃ (1), CBr₃ (2), CCl₃ (3), CH₂Cl (4), CH₃CH₂Cl (5), CF₃ (6)



cis-[Ru^{II}(CH₃CN)₂(1)₂]²⁺

electronic effects of a metal may be used modulate reactivity of 1.

The reported preparation of 4 and 5 from 3 utilized a multistep synthesis specific for monofunctionalized methyl derivatives.^{3b,c} Reductive dehalogenation of 3 with 4 equiv of *n*-Bu₃SnH in benzene yielded 4 (42%) and a minor product, 5, in less but comparable amounts to the overall yield reported previously (4 steps, 68%).^{3b} This synthetic route may allow more substituted derivatives of 1, i.e., sym-tetrachloromethyl and bromomethyl derivatives, to be prepared.

Attempts to synthesize 6 from 2 or 3 by conventional halide exchange reactions⁷ with HF/*N,N'*-dimethylimidazolidinone or SbF₃ in SbCl₃ treated with Cl₂ gas failed to produce any fluorinated product.⁶ A melt of excess SbF₃ and 3 gave 6 in low yield (18%). The physical and spectroscopic properties are consistent with the addition of a trifluoro group to the phenanthroline moiety.^{6,7} The analogous reaction with 2 was unsuccessful. Space-filling

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computer models of 2–6 suggest that the steric bulk of the substituents on 2 and 3 preclude metal coordination, but 4–6 are potential ligands. We are pursuing the metal coordination chemistry and high yield synthesis of 6 and related ligands.

Experimental Section

Solvents and reagents were obtained from commercial sources and used without further purification.

2,9-Bis(trichloromethyl)-1,10-phenanthroline (3) and 2,9-Bis(tribromomethyl)-1,10-phenanthroline (2). A 3-g (13.3 mmol) portion of 1-H₂O and 15 equiv of NBS or NCS were refluxed in CHCl₃ for 6 h. The solution was cooled and filtered. The evaporated filtrate was washed with saturated aqueous Na₂CO₃ and extracted repeatedly with CHCl₃. Drying over anhydrous Na₂CO₃ and chromatography (SiO₂; 2:1 CHCl₃:hexanes) yielded 85–90% of pure 2 or 3: mp(2) 195 °C dec, lit. mp 196–197 °C; mp(3) 214–6 °C as reported. Elemental analysis and ¹H NMR and mass spectral data agreed with literature values.^{3a,b}

2,9-Bis(chloromethyl)-1,10-phenanthroline (4) and 2-(Chloromethyl)-9-methyl-1,10-phenanthroline (5). A 1.50-g (3.6 mmol) portion of 3 was dissolved in 20 mL of benzene (dried over Na/benzophenone ketyl) to which 3.9 mL (14.4 mmol) of *n*-Bu₃SnH and 50 mg of AIBN were added. The solution was refluxed under Ar for 2 h until complete (TLC, 2:1 petroleum ether:EtOAc). The reaction was quenched with aqueous Na₂CO₃ and extracted with CHCl₃. The combined CHCl₃ extracts were dried over anhydrous Na₂CO₃, evaporated, and purified by chromatography

(SiO₂; 2:1 petroleum ether:EtOAc) to yield 0.42 g of 4 (42%) and 0.13 g of 5 (14%): ¹H NMR and mass spectral data agreed with literature values.^{3a,b}

2,9-Bis(trifluoromethyl)-1,10-phenanthroline (6). A 0.3-g (1.25 mmol) portion of 3 (mp 214–6 °C) and 3.0 g (16.8 mmol) of SbF₃ (dec 235 °C) were ground in a mortar and pestle and then placed in a 25-mL round-bottom flask fitted with a reflux condenser under N₂. The contents of the flask were gently heated with a Bunsen burner with agitation until a melt formed. Heating and agitation were maintained for 10 min; some charring and decomposition of the SbF₃ occurred. After cooling, the solids were washed with water and neutralized with aqueous NaOH. This mixture was washed repeatedly with ethyl acetate. The washings were combined, dried over anhydrous Na₂CO₃, and evaporated. Chromatography (SiO₂; CH₂Cl₂) yielded 0.040 g of 6 (18%) as a white powder: mp 164–6 °C; MS, *m/z* 316 (M⁺), 247 (M⁺ – CF₃); ¹H NMR (CDCl₃, 300 MHz) δ 8.00 (s, H5, 6, 2 H), 8.05 (d, H3, 8, *J* = 8.5 Hz, 2 H), 8.51 (d, H4, 7, *J* = 8.5 Hz, 2 H) vs TMS; ¹⁹F NMR (d₆-DMSO, 282 MHz) δ –65.0 vs CFCl₃. Anal. Calcd for C₁₄H₆N₂F₆: C, 53.18; H, 1.61; N, 8.86. Found: C, 52.96; H, 1.51; N, 8.93.

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